



Experimental investigations on the electrochemical and thermal behaviour of LiCoPO₄-based cathode

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HIGHLIGHTS

- The two-step mechanism during charging/discharging LiCoPO₄ cathodes is illustrated.
- Thermal stability of LiCoPO₄ cathodes with various states of charge is reported.
- Partially charged LiCoPO₄ thermally stable up to 480 °C.
- Fully charged LiCoPO₄ decomposes between 150 and 200 °C under release of O₂ and CO₂.
- Electrolyte and crystallite size influence the decomposition temperature.

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ABSTRACT

LiCoPO₄ based cathodes have been investigated in matter of electrochemical performance and thermal stability. The two-step characteristic of the charging process of LiCoPO₄ cathodes is clearly illustrated. Investigations on the thermal stability of the partially delithiated and the fully delithiated cathode were performed by using simultaneous DSC-TG-MS. While the partially delithiated cathode shows a high thermal stability, the fully charged cathode decomposes between 160 and 260 °C. Furthermore, the influence of electrolyte, carbon coating and conductive additives on the decomposition temperature is discussed as well as the influence of the crystallite size of LiCoPO₄.

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1. Introduction

Using lithium-ion batteries in applications such as hybrid electric vehicles (HEV) or electric vehicles (EV) would have an important impact in the future of the environment by improving energy efficiency and reducing pollution. Nevertheless to make lithium-ion batteries suitable for those large scale applications two main challenges have to be optimized: energy density and safety. Although lithium-ion batteries are generally safe, various hazards can occur under abuse conditions like mechanical penetration, electric abuse or external heat input. All these kinds of abuse lead to an increasing temperature in the cell and can be followed by the decomposition of the active material and a “thermal runaway” of the cell. One way to improve safety is to increase the thermal

stability of the active materials in particular the stability of the cathode.

For these reasons the lithium transition metal phosphates LMPO₄ (M = Fe, Mn, Co, Ni) attracted attention since Padhi et al. reported in 1997 the reversible electrochemical extraction of lithium from LiFePO₄ [1]. Especially LiFePO₄ has been extensively studied in the last years by many research groups [1–4]. It shows a high thermal stability (even in the charged state) and a reversible theoretical capacity that is comparable to LiCoO₂ [1,3]. The main drawback of LiFePO₄ is the lower energy density because of the low charge/discharge potential. From this point of view LiCoPO₄ is a very attractive material due to its high discharge potential of 4.8 V vs. Li/Li⁺ and the resulting higher energy density [5–8]. Recently several groups have demonstrated that the electrochemical performance of the LiCoPO₄ depends sensitively on composition, particle morphology and carbon coating. Some improvements have been observed by partial substitution of Co by Fe or V [9–14].

LiCoPO₄ crystallises in the olivine structure, similar to the other transition metal phosphates. However, first experimental results of

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Bramnik et al. and theoretical calculations of Hautier et al. show a much lower thermal stability of delithiated LiCoPO_4 as expected for phospho-olivines [15,16].

Generally one would assume a similar mechanism for the phase transition LMP/MP for all those transition metals. Interestingly the lithium insertion and deinsertion of lithium in LiCoPO_4 seems to differ from the better known LiFePO_4 and LiMnPO_4 . Recent studies report that it proceeds in a two step mechanism indicating an additional defined intermediate phase. Up to now only two groups discussed this behaviour in more detail [6,17].

In this paper we report about investigations on the intermediate phase using thermal analysis of partially charged LCP cathodes. Furthermore we determined the influence of factors like crystallite size, electrolyte and surface coating on the thermal stability of the different phases.

2. Experimental

The synthesis for LiCoPO_4 is performed in a two step route. In the first step the precursor $\text{Li}_3\text{PO}_4/\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ was obtained by coprecipitation method starting from CoSO_4 and LiOH in H_3PO_4 . After the precipitate was filtered and washed, an aqueous solution of lactose-monohydrate was given to the filter cake. The end product Lithium cobalt phosphate (LCP) was obtained by a solid-state reaction. Therefore the precursor was annealed under argon at 500 °C, 650 °C and 700° respectively to obtain samples with different crystallite sizes. These carbon coated samples are henceforth referred as C500, C650 and C700. For comparison also an additional LCP material without additional carbon coating was used (carbon content <0.1%, referred as CF sample). All materials contained a small excess of Li_3PO_4 , quantified by XRD, and listed in Table 1.

The electrodes were manufactured by preparing a slurry including Super-P (carbon black) and KS6 (graphite) as conductive additives and polyvinylidene fluoride (PVDF) as binder. The composition was: $\text{LiCoPO}_4:\text{Super-P:KS6:PVDF} = 84:4:4:8$ wt%. N-Methyl-2-pyrrolidone (NMP) was used as solvent. The slurry was coated on an aluminium foil using the “doctor blade” technique (thickness 250 μm of wet film) and dried at 80 °C/1 h. Circular electrodes were punched from the foil, pressed for better contact between material and aluminium current collector and were dried over night at 130 °C under vacuum.

For electrochemical measurements three electrode T-Cells were used with lithium as counter and reference electrode, LiCoPO_4 as working electrode, glass microfiber (Whatman, GF/A) separator and 1 M LiPF_6 in EC:DMC (1:1wt%) (UBE Industry, Japan) as electrolyte. The cells were assembled in an argon filled glove box ($\text{O}_2/\text{H}_2\text{O} < 0.1$ ppm).

Galvanostatic measurements were carried out at room temperature using a Maccor Serie 4000 galvanostate. The LiCoPO_4 electrodes were cycled between 3.0 V and 5.3 V with a C/20 rate.

Table 1

Annealing temperature, average crystallite size and composition of the different active materials. Additionally onset and peak maximum temperature of the decomposition of charged LiCoPO_4 cathodes.

	CF	C500	C650	C700
Annealing temp. [°C]		500	650	700
Crystallite size $\bar{\phi}$ [nm]	79.6(24)	36.3(11)	63.2(20)	98.3(37)
LiCoPO_4 [%]	89.59(42)	87.62(60)	90.28(44)	86.95(51)
Li_3PO_4 [%]	8.88(42)	11.55(59)	8.76(44)	10.86(47)
Co^0 [%]	—	0.83(12)	0.958(82)	0.550(81)
Onset PeakA [°C]	162/215	135	150	166
Max. PeakA [°C]	242	167	190	190–240

The charged and cycled cells were disassembled in an argon filled glove box for further analysis. For the thermal analysis some electrodes were rinsed several times with dimethyl carbonate (DMC) and dried in the glove box under vacuum. To investigate the influence of the electrolyte some electrodes were punched without rinsing and drying and were quickly sealed in an aluminium pan. The thermal analysis was performed using a STA 449C Jupiter differential scanning calorimeter combined with a QMS 403 C Aëlos quadrupol mass spectrometer (both Netzsch). Before starting the measurement, the pan was pierced with a cannula. The DSC-TG measurements were carried out in argon atmosphere, with Al_2O_3 in an aluminium pan as reference and a heating rate of 10 °C min⁻¹. The temperature range was set to 30–550 °C. A slight argon stream carried the volatile components directly to the MS during the whole measurement.

XRD pattern were measured with a Bruker D5000 X-Ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) operating at 40 kV and 40 mA. For ICP measurements a SPECTRO Arcos SOP spectrometer was used.

3. Results and discussion

For basic characterisation the pristine LiCoPO_4 active material was measured by X-ray diffraction. LiCoPO_4 olivine was identified as the main phase using Topas (WPPD method) for evaluation. In addition a small amount of metallic cobalt and about 7 wt.% Li_3PO_4 were detected as impurity phases (Table 1). Cell parameters of $a = 10.2008(6) \text{ \AA}$, $b = 5.9250(4) \text{ \AA}$ and $c = 4.7008(3) \text{ \AA}$ match with the data in literature [5,15]. The averaged crystallite size of the different materials could also be determined by XRD measurement (Table 1).

3.1. Electrochemical performance

The specific theoretical capacity of LCP was calculated to 160 mAh g⁻¹ from the analytically determined cobalt content under the approximation that all cobalt is crystallised in the olivine structure.

Fig. 1 shows the potential curves of LiCoPO_4 for the first cycle. The specific charge of 190 mAh g⁻¹ was measured during the initial charge up to 5.3 V vs. Li/Li^+ . That corresponds to 120% of the theoretical capacity for the $\text{Co}^{II}/\text{Co}^{III}$ step. Therefore some electrolyte side reactions took place as for olivines 100% charged means fully delithiated in contrast to the lithium transition metal oxides

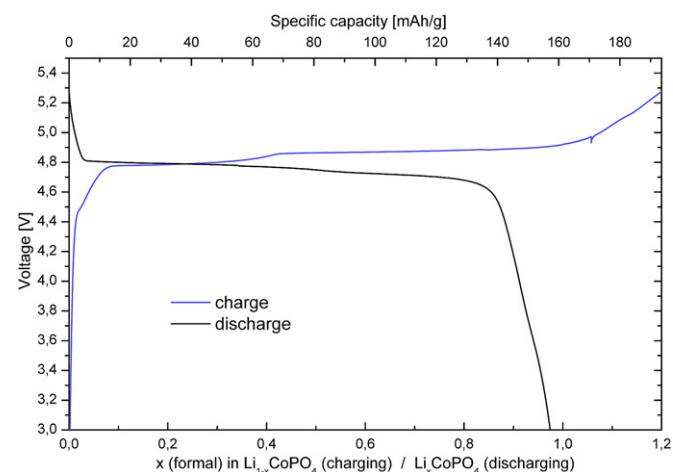


Fig. 1. Galvanostatic charge and discharge curve for a LiCoPO_4 based cathode at a rate of C/20.

that can be overcharged as lithium remains in their structure even at “full charge”. Electrolyte decomposition due to the high voltage and the slow cycling rate (C/20) explains the excess of measured charge capacity. During the first discharge 98% (156 mAh g⁻¹) of the theoretical value could be reached. Thus almost the whole active material is utilised for intercalation/deintercalation during the first cycle.

Furthermore the charging curve clearly shows two plateaus indicating that three phases are involved in the charging progress. That the charging of LiCoPO₄ proceeds in a two-step-mechanism was already described in literature [6,17]. Bramnik et al. reported that a partially delithiated phase, named Li₂CoPO₄, is formed during the first plateau. Within the second plateau the complete delithiated phase CoPO₄ is formed.

The incremental plot of the first cycle (Fig. 2) shows the two-step character even clearer. Thereby the plateaus during charging can be localised at 4.78 V and 4.87 V respectively. Furthermore this plot confirms the reversibility of the deintercalation reactions. Although the two plateaus can hardly be seen in the discharge potential curve, the derivation of the charge with respect to the potential clearly reveals the two steps also during discharging. In addition these two reduction peaks are only slightly shifted to lower potential (4.72 V and 4.79 V) related to their corresponding oxidation peaks during charging. This small hysteresis of around 60 mV is ascribed to a fast kinetic.

3.2. Thermal stability according to the state of charge

Few investigations on the thermal stability of charged LiCoPO₄ and the decomposition mechanism of the delithiated phases are published in literature up to now. Bramnik et al. [15] showed that the synchrotron pattern for Li₂CoPO₄ and CoPO₄ disappear within the temperature range of 90–160 °C. DSC-TG measurements show a slight exothermic peak and a mass loss beyond 200 °C. These results differ from the DSC-measurement of Okada et al. They found an exothermic decomposition of LiCoPO₄ at 290 °C. Additionally Hautier et al. [16] computed the thermal stability of Co(III)-phosphate. Their calculations reveal a significantly lower thermal stability of charged LiMPO₄ (M = Mn, Co, Ni) compared to LiFePO₄ in the following trend: LiFePO₄ > LiMnPO₄ > LiCoPO₄ > LiNiPO₄. But the partially delithiated Li₂CoPO₄ phase was not considered.

Our approach was the investigation on the LiCoPO₄/Li₂CoPO₄/CoPO₄ system at different states of charge by thermal analysis with especial consideration of the intermediate phase Li₂CoPO₄ and its influence on the thermal stability of the electrode.

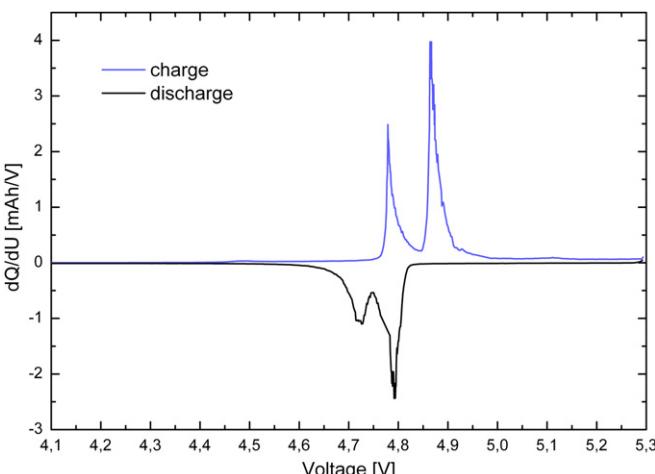


Fig. 2. Incremental plot of the first cycle of a LiCoPO₄ based cathode.

Therefore several cathodes were charged up to defined points of charge in the charging characteristic (shown in Fig. 3). The LiCoPO₄ → Li₂CoPO₄ step in the charging curve was used as point of reference. Due to the most reproducible electrochemical behaviour and the sharpest plateaus of the four investigated materials, the CF material was used for following measurements. The electrodes were rinsed and dried before thermal analysis to detect the thermal decomposition without influence of the electrolyte.

Fig. 4 shows the DSC and TG profiles of the cathodes charged to different SOC. The pristine electrode (I) shows only the melting (Peak M, 170 °C) and the decomposition (Peak C, 480 °C) of the binder. As expected untreated LiCoPO₄ cathodes are thermally stable up to high temperature. The samples that were charged to the beginning (electrode II) and to the end (electrode III) of the first plateau still do not show any exothermic reaction except the decomposition of the binder. Contrary to the results of Bramnik et al. these investigations show that the Li₂CoPO₄ phase, built during the first plateau, is thermally stable at least up to 550 °C.

Cathode IV, charged to the beginning of the second plateau, shows an exothermic response in the DSC curve. Two exothermic peaks (A' and A) could be observed between 160 °C and 260 °C. With higher state of charge along the second plateau, the amount of complete delithiated CoPO₄ increases successively. Analogous the enthalpy of the exothermic peaks and the mass loss are increasing with higher state of charge (curves V, VI and VII). The exothermic enthalpy of the reaction for the fully charged cathode could be determined to 162 J g⁻¹. Hence the exothermic behaviour corresponds to the thermal instability of the delithiated CoPO₄ phase. Peak C can be referred to the binder as pristine PVDF decomposes exothermally in the same temperature range. But in curves V–VII this peaks seems to be overlaid by another exothermic peak which we could not identify yet.

3.3. Decomposition mechanism/influence of carbon

Another safety risk beside heat generation during decomposition is the evolution of oxygen gas. Several authors report about this topic. Hautier et al. [16] investigated the thermal stability of CoPO₄ by calculating the critical oxygen chemical potential at which the charged material begins to evolve oxygen gas. The results show that Co(III)-phosphate seems to be much more unsafe compared with FePO₄ or MnPO₄. Their computations result in a decomposition to Co₃(PO₄)₂, Co(PO₃)₂ and oxygen gas. Bramnik et al. suppose the decomposition to Co₂P₂O₇ under release of

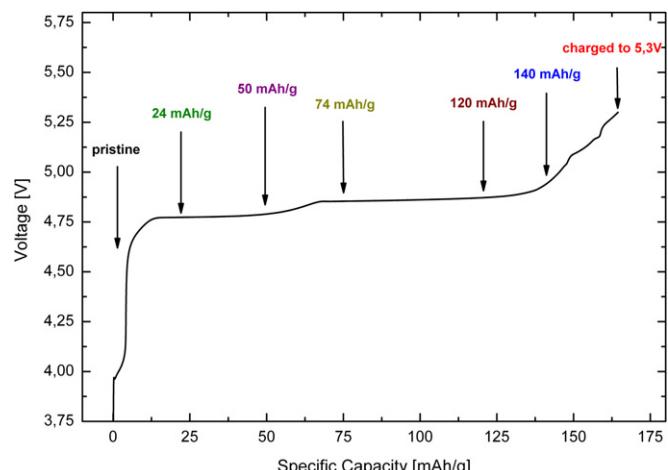


Fig. 3. First charging of a LiCoPO₄ cathode vs. lithium.

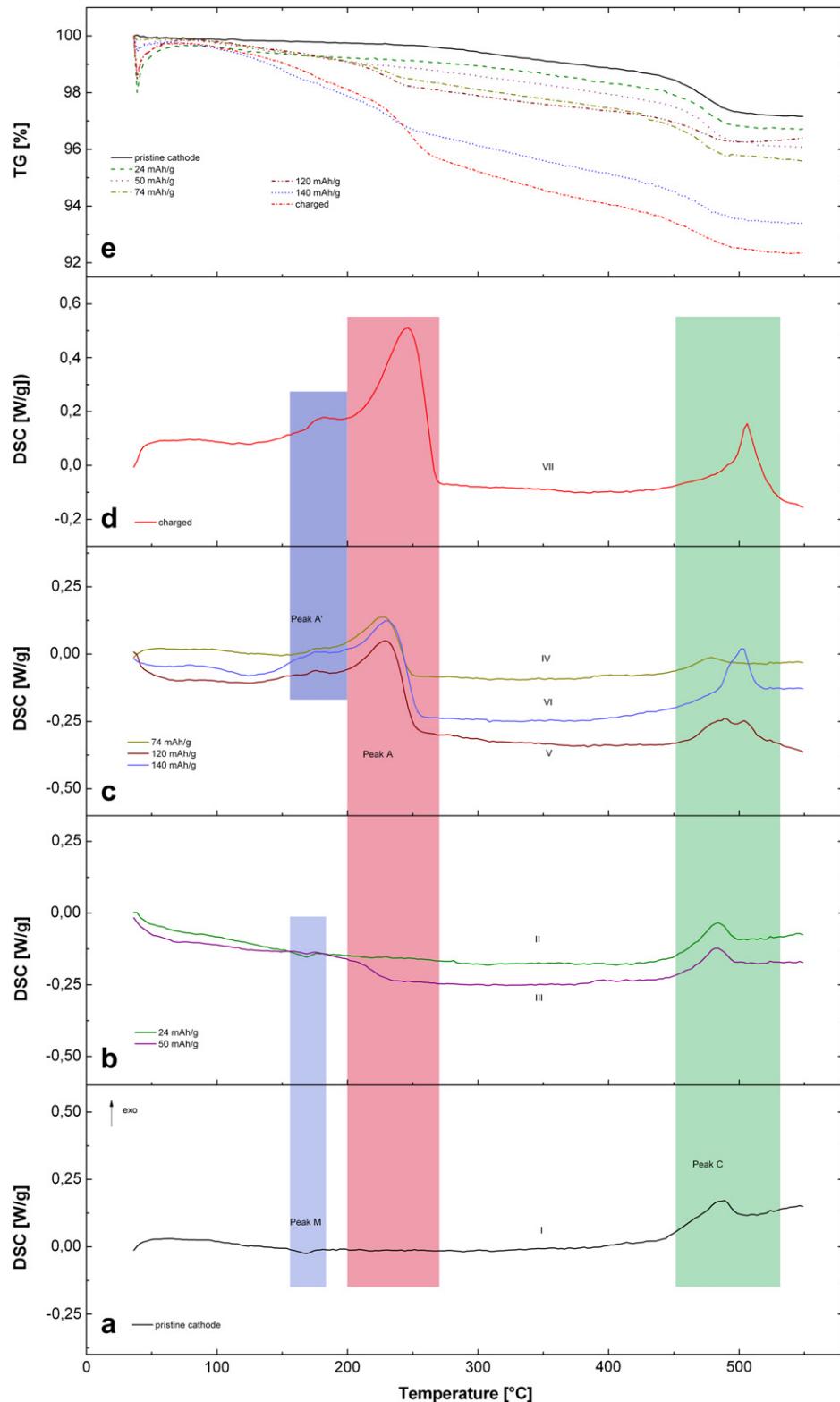
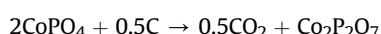


Fig. 4. (a-d) DSC profiles of rinsed and dried LiCoPO₄ cathodes with different states of charge. (e) TG curves of these cathodes.

oxygen. Furthermore a direct reduction with present carbon is possible. They predict the following decomposition mechanisms:



With simultaneous mass spectrometry it was possible to detect the volatile decomposition products to get a deeper understanding about the proceeding reactions.

Fig. 5 shows the DSC and TG profiles of charged cathodes (5.3 V) built with two different active materials: C600 (coated with carbon, 3%wt. assessed at synthesis) and CF (only marginal amount of

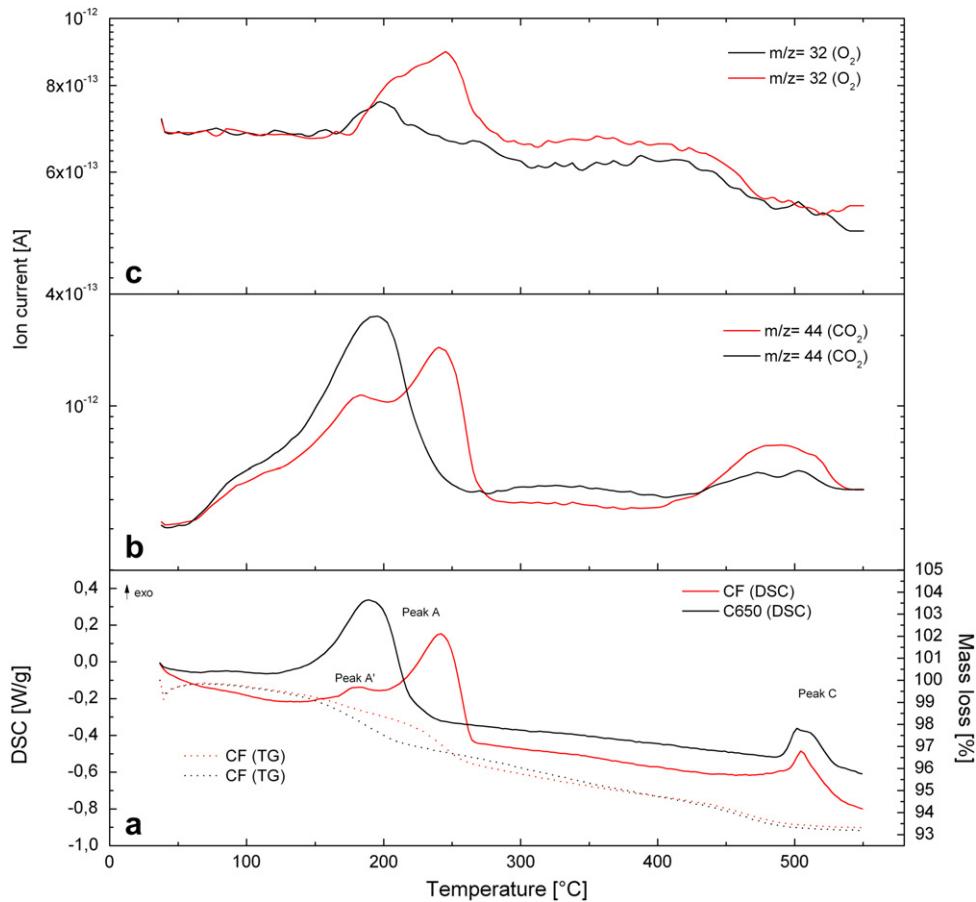


Fig. 5. (a) DSC-TG profile of a charged CF (red) and C650 (black) cathode and simultaneous MS signal of CO₂ (b) and O₂ (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coated carbon). The cathodes were rinsed and dried before thermal analysis.

Both, O₂ and CO₂, could be detected for each electrode exactly in the temperature range where the decomposition takes place. With respect to the scaling one can see that the amount of released CO₂ is significantly higher than the amount of O₂ in both cases. That leads to the assumption that the direct reduction of Co(III)-phosphate by carbon is the main reaction path.

However the main decomposition peak corresponding to the CF material is shifted to higher temperatures (values listed in Table 1).

An explanation for this effect can be drawn from the nature of the carbon present in the electrode. Two different species of carbon are available that can take an active part in the reaction: the carbon coating on the surface of LiCoPO₄ and the conductive additives (graphite and carbon black) of the electrode mixture. The carbon coating, formed on the surface of the material during the annealing process of the precursor, has a very small thickness (5–10 nm) and a very tight contact to the active material. Therefore both availability and reactivity of the carbon coating are given. On the other hand the conductive additives (graphite and carbon black) have rather point contact with the LiCoPO₄ particles. This is sufficient for electrical contact in the electrochemical cell but not for the chemical reaction of solids. According to the lower availability the conductive additive shows a lower reactivity.

In the CF cathode the small amount of coated carbon (0.1%) can only partially promote the decomposition of the active material, leading to the small PeakA' at 180 °C. The residual CoPO₄ reacts at higher temperatures with the conductive additives (242 °C, PeakA).

In addition to that the amount of released oxygen is higher for the CF cathode as well (Fig. 5c) due to the lower reactivity of the conductive additives. Hence on the one hand carbon coating seems to decrease the decomposition temperature on the other hand it decreases the release of oxygen.

3.4. Influence of the electrolyte

Beside these two pure carbon species, the electrolyte is an additional carbon source that can be directly oxidised during the decomposition of the active material. As the electrolyte wets the surface of the LiCoPO₄ particles it is in good contact to the material. In contrast to the solid carbon sources like coated carbon or conductive additives, new electrolyte can continuously diffuse to the decomposing active material and replace the reacted electrolyte. Therefore the electrolyte should show a high reactivity. Nevertheless as the boiling points of the solvents DMC (90 °C) and EC (248 °C) lay in the temperature range of the decomposition reaction the endothermic vaporisation possibly overlays the exothermic signal of the decomposition.

Fig. 6 shows a comparison of the DSC-TG-MS measurements of a dry LiCoPO₄ cathode and a cathode with electrolyte, both built with C650 material and charged up to 5.3 V. The exothermic PeakA of the electrode soaked with electrolyte is shifted to a significantly lower temperature (onset: 98 °C, max.: 156 °C), indicating a high influence of the electrolyte on the decomposition. The endothermic PeakB at 260 °C, accompanied by a high mass loss, is related to the evaporation of ethylene carbonate (EC) and the decomposition of

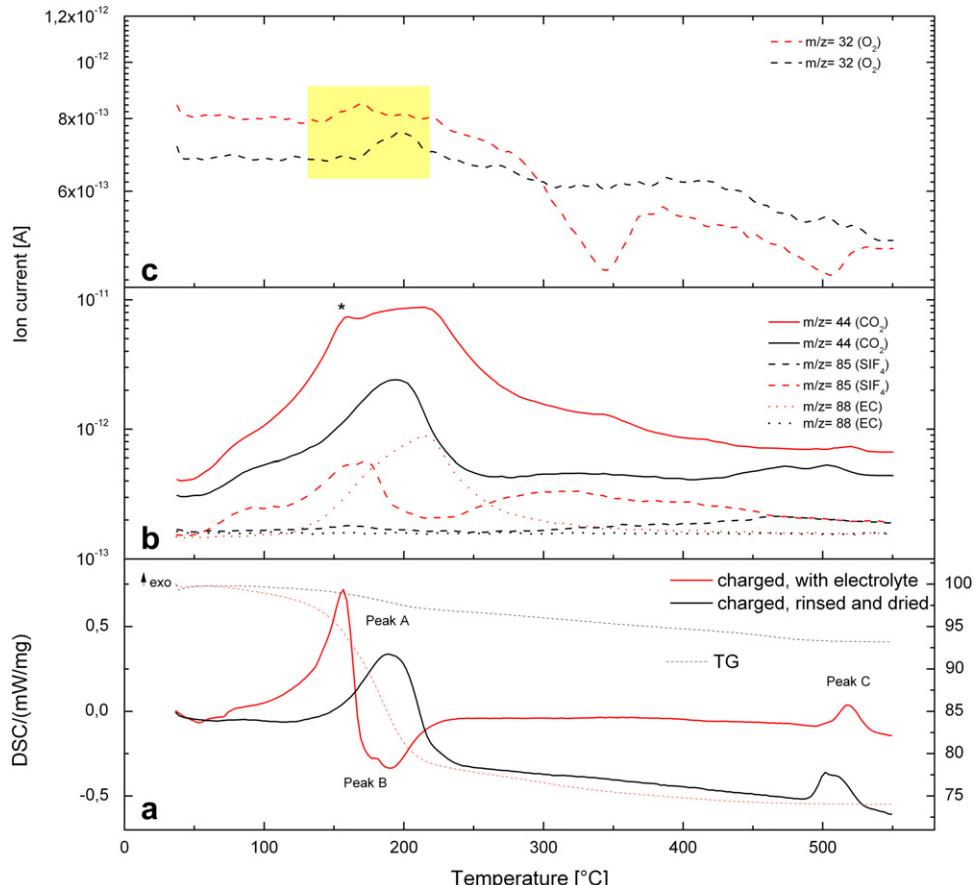


Fig. 6. TGA-MS-profile of a LiCoPO_4 cathode with electrolyte (red) compared to a rinsed and dried cathode (black), both charged up to 5.3 V. (a) DSC-TG-profile, (b) mass signals of EC, CO_2 and SiF_4 and (c) mass signals of O_2 . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the conductive salt LiPF_6 . That could be traced by the MS signals of specific fragments (Fig. 6b). Ethylene carbonate ($m/z = 88$) as well as CO_2 ($m/z = 44$) is detected between 120 °C and 270 °C. This is the temperature range in which the evaporation of the electrolyte solvent takes place. Although CO_2 is a main fragment of ethylene carbonate, the side peak at around 150 °C (marked by *) in the CO_2 signal cannot be related to EC as it is not occurring in the $m/z = 88$ signal. That indicates an increased release of CO_2 during the exothermic reaction that is not solely caused by the solvent volatilisation but superposed by it.

The mass signal $m/z = 85$ can be related to SiF_3 , the main fragment of SiF_4 . The conductive salt LiPF_6 is quite unstable and decomposes at higher temperatures to LiF and PF_5 or at presence of water to LiF , POF_3 and HF [18]. In the transfer capillary SiF_4 can be formed by the reaction of HF [19] and PF_5 with the glass layer which explains the detection of the main fragment SiF_3 ($m/z = 85$). Thus the signal of SiF_3 is an indirect evidence of the decomposition of the conductive salt. Therefore this decomposition can indirectly be deduced even though the DSC signal is overlaid by the endothermic evaporation of EC. Compared to literature [18] and our own measurements of uncharged electrodes soaked with electrolyte, the decomposition of the conductive salt is also shifted to a lower temperature. Furthermore a slight release of oxygen gas while decomposing the wet electrode could be detected as well (Fig. 6c). In summary all present carbon sources contribute to the thermal decomposition of charged LCP. Nevertheless the reactivity of the different carbon sources is staggered due to their availability: electrolyte > carbon coating > carbon additive.

3.5. Influence of the crystallite size

The electrochemical performance of cathode materials is decisively influenced by the material synthesis and the resulting physical parameters like crystallite size or crystallinity. This is shown in literature for almost every material, also for LiCoPO_4 [6,7]. We investigated if the crystallite size also has an impact on the thermal stability.

As mentioned in the experimental part, the annealing temperature of the precursor was varied to obtain different active materials. The materials C500, C650 and C700 differ in the amount of impurity phases and the averaged crystallite sizes, calculated from XRD measurements and listed in Table 1.

Fig. 7 shows the DSC and TG profiles of charged cathodes (5.3 V) built with the different active materials. All these cathodes were rinsed and dried before the thermal analysis. A considerable difference of the decomposition temperatures can clearly be seen. However the detected impurity phases do not influence the decomposition since Li_3PO_4 is thermally stable up to temperatures higher than 500 °C [20] and other impurity phases are only present in marginal amounts. Therefore the shift of the peaks can probably be correlated with the different crystallite size. As shown in Table 1 the averaged crystallite size increases with the annealing temperature. The trend of the crystallite size matches with the shift of the decomposition temperature for the three carbon coated materials: the charged C500 material, annealed at low temperature, already decomposes at 167 °C (onset 135 °C). The DSC and TG profiles of the C650 and C700 cathodes show that the decomposition temperature

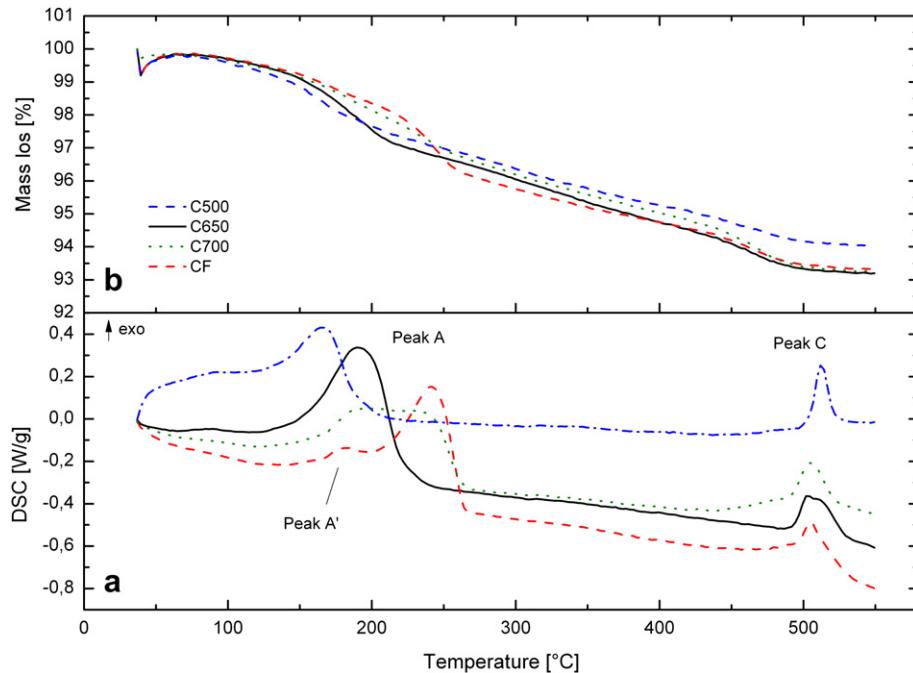


Fig. 7. DSC (a) and TG (b) profiles of LiCoPO_4 cathodes based on material with different crystallite sizes.

shifts to higher values with increasing crystallites. This behaviour was also observed for NCA cathodes by Albrecht et al. [21].

However only the onset of the small PeakA' (162 °C) of the CF cathode fits in this trend. The main decomposition takes part at higher temperatures. Therefore the reactivity difference of the carbon species (as mentioned before) has more influence on the thermal stability of the composite than the crystallite size.

4. Conclusions

The electrochemical curves of LiCoPO_4 display clearly the two-step characteristic of the charging and discharging process. That indicates a defined intermediate phase occurring during intercalation and deintercalation of lithium.

Thermal analysis of partially charged LiCoPO_4 cathodes shows a crucial difference of the thermal stability of the partially delithiated Li_2CoPO_4 and the completely delithiated CoPO_4 . While Li_2CoPO_4 shows no exothermic response when heated up to 550 °C, the CoPO_4 phase decomposes between 160 and 260 °C under heat evolution. Therefore the thermal instability of charged LiCoPO_4 can be ascribed to the delithiated CoPO_4 phase.

With simultaneous mass spectrometry it was possible to confirm the assumption of Bramnik et al. [15] that the decomposition of CoPO_4 proceeds under evolution of O_2 and CO_2 gas. Although the main reaction pathway is the direct oxidation of present carbon, leading to high amounts of CO_2 , the small amount of released O_2 must be taken into consideration. By comparing coated with uncoated and wet with dry electrodes the reactivity of the various carbon sources could be determined: The electrolyte as carbon source shows the highest reactivity and leads therefore to the lowest decomposition temperature (160 °C). For dry electrodes with carbon coating the decomposition temperature increases to 190 °C. The highest thermal stability is given by the dry electrodes without carbon coating, indicating that the conductive additives, as the only remaining carbon source show the lowest reactivity. The crystallite size affects the decomposition temperature as well.

Increasing the crystallite size raises the decomposition temperature for up to 70 °C.

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